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[4] Impact resistant polystyrene/polyolefin compositions and grease resistant articles formed therefrom.

(57) A composition consisting essentially of a) high impact styrene-butadiene graft copolymer or a mixture thereof with no more than about 55% styrene homopolymer, b) small proportions of polyethylene or polypropylene, and c) a block copolymer X-Y-X, in which each X is a polystyrene block of about 5,000 to 10,000 molecular weight and Y is a hydrogenated polybutadiene block of 25,000 to 50,000 molecular weight, is suitable for the moulding of shaped articles which are resistant to attack by fatty substances and chemicals, and which have impact resistance comparable to high impact polystyrene. The articles are characterized by having a skin which is substantially enriched in polyolefin.

IMPACT RESISTANT POLYSTYRENE/POLYOLEFIN COMPOSITIONS AND GREASE RESISTANT ARTICLES FORMED THEREFROM

This invention relates to improved impact resistant polystyrene compositions, and to articles produced therefrom.

Polystyrene is an economically priced thermoplastic material having many desirable properties. For a variety of uses polystyrene is employed as an impact-improved product, made as a graft polymer of styrene and an elastomer, typically a butadiene-containing polymer, particularly polybutadiene.

An undesirable property of polystyrene is its tendency to deteriorate drastically under the influence of materials which induce stress-cracking, such as fatty substances, e.g., fatty foodstuffs. The deterioration is manifested by surface crazing of polystyrene articles and drastic loss of impact strength of articles made from impact-improved polystyrene compositions. Some major fields of use have been foreclosed to polystyrene because of these disadvantages. Styrene copolymers such as ABS (a copolymer of acrylonitrile, butadiene and styrene) are conventionally used where resistance to chemically induced stress cracking is required, such as in containers for fatty foodstuffs.

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It is known that blends of polystyrene and polyolefins generally have very poor impact properties because the polymers tend to form separate domains within an article, so that articles formed from such blends delaminate under stress.

It has been taught that certain materials, and particularly certain block copolymers, can be employed to improve the compatibility of styrenic and olefinic polymers in blends. Thus, U.S. Patent No. 3,894,117 describes compositions containing a major proportion of polyolefin, a small proportion of polystyrene and proportion of polystyrene-polyolefin copolymer to improve their a two-block polystyrene-polyolefin copolymer to improve their compatibility, primarily for the purpose of improving the impact characteristics of the polymer and also to produce a paper substitute.

A series of BASF patent cases illustrates a gradual evolution of concepts dealing with the use of certain block copolymers. 10 U.S. Patent 4,013,166 is broadly directed to the use of a variety of different vinyl aromatic/diene copolymers in admixture with a polyolefin as additives blended with styrene homopolymer to provide impact-improved polystyrene which is said to be superior in rubber utilization to conventional polystyrene/elastomer blends and 15 superior in gloss to graft polymerized high impact polystyrene. U.S. Patent 3,738,907 and U.K. Patent 1,363,466 are directed to using two-block copolymers of polystyrene and hydrogenated diolefin, primarily as adhesion promoters for laminates and also to provide compatibility of polystyrene and polyolefins. German OLS 20 2,236,903 broadly discloses the use of block copolymers, again for the purpose of providing adhesion-promoting compositions.

The primary object of this invention is to provide a thermoplastic composition consisting predominantly of polystyrene and which can be formed into articles having both the impact resistance of impact-improved polystyrene and also the desirable resistance to chemically induced stress cracking which characterizes the more expensive styrene copolymers such as ABS.

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The compositions of this invention consist essentially of (A) 60-93 parts by weight, per 100 parts of the composition, of a polystyrene component consisting of 100 to 45% by wt. of a thermoplastic styrene-diolefin elastomer graft copolymer with 0 to 55% by wt. of thermoplastic styrene homopolymer;

(B) 2 to 30 parts by weight, per 100 parts of the composition, of polyethylene or polypropylene; and (C) 5 to 20 parts by weight, per 100 parts of the composition, of a block copolymer X-Y-X, where each X is a polystyrene block of 5,000 to 10,000 molecular weight and Y is a hydrogenated polybutadiene block of 25,000 to 50,000 molecular weight, the total molecular weight of the block copolymer being less than 60,000.

The compositions of this invention consist essentially of the polystyrene graft copolymer component "A", the polyolefin component "B", and the block copolymer component "C". In addition, these compositions may contain conventional additives, such as stabilizers, dyes, pigments, fillers or the like.

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Component "A", in one embodiment, is a graft copolymer of styrene and an impact-improving elastomer, such as butadiene or a butadiene-containing elastomer. Such impact-improved polystyrene compositions are commercially available materials. Their methods of preparation and properties are well known. They are conventionally designated "high impact polystyrene", abbreviated "HIPS". The elastomer content of HIPS is typically in the range of 5-15% by wt, basis styrene, and is present as dispersed particles containing occluded polystyrene. The compositions may contain minor amounts of substituted vinyl aromatic compounds copolymerized with the styrene.

In an alternative embodiment, component "A" is a mixture of at least 45% of high impact polystyrene graft copolymer, as described above, with up to 55% of styrene homopolymer.

For further information on the properties and preparation both of styrene homopolymer (i.e., polystyrene) and of HIPS, reference is made to the article on "Styrene Plastics" in Volume 19 of Kirk-Othmer "Encyclopedia of Chemical Technology", pages 85-134, (1969), and the references cited therein.

For purpose of this invention, the characteristics of the HIPS, and of the polystyrene (PS) if used, are preferably within the following ranges:

	HIPS Suit- able		PS Suit- Pre- able ferred
Elastomer, % by wt.	5–12	6–8	0 0
Izod impact (Joules/ 2.54 cm notch)	≥1.5	∿2.0	~0.254 ~0.25 ⁴
Tensile yield strength,	>,20	≥ ²⁴	>,40 >,50
Vicat softening temper-			
ature, ^O C for extrusion for injection moulding	>99 >85	≥102 ≥ 93	>99 >102 >85 > 93
Melt index (condition C. 200°C) for extrusion for injection moulding	1.5-4 5-15	1.5 - 3 6-10	1-4 1-3 5-25 10-20

Component "B" is low-density or high-density polyethylene or polypropylene. Each of these polyolefins is a commercially available material; their methods of preparation and properties are well-known as illustrated in the article on "Olefin Polymers" in Volume 14 of Kirk-Othmer "Encyclopedia of Chemical Technology", pages 217-335 (1967).

High density polyethylene has an approximate crystallinity of over about 75% and density of between about 940 and 970 kg/m 3 while low density polyethylene has an approximate crystallinity of over about 35% and a density of between about 900 and 940 kg/m 3 . Most commercial polyethylenes have a number average molecular weight of about 50,000 to about 500,000.

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The polypropylene used in the compositions of this invention should desirably consist predominantly of so-called isotactic polypropylene, as opposed to atactic polypropylene. The number average molecular weight of the polypropylene employed is typically in excess of about 100,000. Polypropylene is commercially characterized primarily by its melt flow range, which varies

with its molecular weight range. Polypropylenes with melt flow index values in the range from 0.6 to 12 (as measured by ASTM method D-1238-70) are suitable for use in this invention.

Component "C" is a block copolymer X-Y-X. X represents polystyrene blocks and Y represents a hydrogenated polybutadiene block. Such copolymers are preferably produced by first making a precursor block copolymer X-Y'-X in which Y' is polybutadiene and subsequently hydrogenating the block copolymer to substantially saturate the centre block without significantly saturating the styrene polymer blocks. Block copolymers of this type and their 10 methods of preparation are well known. They are described in greater detail, for example, in U.S. Patent No. 3,595,942, which also describes their preparation, including suitable methods for the hydrogenation of the precursor polymers. The structure of the polymers is determined by their methods of polymerization. Linear polymers X-Y'-X are produced by sequential introduction of the 15 desired monomers into the reaction vessel when using such initiators as lithium-alkyls or dilithiosilbene and the like, or by coupling a two segment block copolymer with a difunctional coupling agent. The presence of any coupling residues in the polymers may be ignored for an adequate description of the polymers forming a part 20 of the compositions of this invention. Likewise, in the generic sense, the specific structures also may be ignored. It is preferred that between about 35 and about 55 mol.% of the condensed butadiene units in the butadiene polymer block of the precursor polymer have 1,2-configuration. A typical, useful proportion of 25 1,2-structure is about 40%. When such a block is hydrogenated, the resulting product is identical to, or resembles, a copolymer block of ethylene and butene-1. Such a polymer, with polystyrene end blocks, may be designated an "S-EB-S" block polymer. A preferred polymer for this invention is an S-EB-S polymer in which 30 the molecular weight of the S-blocks is about 7,500 and that of the EB-block about 37,000, being designated "7.5S-37EB-7.5S". The molecular weight of the blocks is determined by gel permeation chromatography. 35

Hydrogenation of the precursor block copolymers is preferably effected by use of a catalyst comprising the reaction products of an aluminium alkyl compound with nickel or cobalt carboxylates or alkoxides under such conditions as to achieve substantially complete hydrogenation of at least 90% of the aliphatic double bonds while hydrogenating at most a small proportion of the alkenyl arene aromatic double bonds. Preferred block copolymers are those in which at least 99% of the aliphatic double bonds are hydrogenated while less than 5% of the aromatic double bonds are hydrogenated.

The block copolymers X-Y-X used in the compositions of this invention should have relatively low molecular weights within the limits defined above.

In the compositions utilized in this invention, the above components may be present in the following proportions, expressed as parts per hundred parts by weight of total components A, B

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	and C:		Preferred	Most preferred
	and or	Maximum range	Prercur	-(0) norts
	_	60-93 parts	70-85 parts	•
	Component "A":		5-20 parts	8-12 parts
	, upu.	2-30 parts	- •	0 10 parts
	Component "B":		8-15 parts	0212 par
	Component "C":	5-20 parts		forehly if
20	Component	. "" +0	Component "B"	is preferably in

The ratio of Component "C" to Component "B" is preferably in the range of from 0.5:1 to 2:1, and preferably about 1:1.

It is known to persons skilled in the art of manufacturing plastic articles that different methods of manufacture require polymers having different melt properties. For example, polymers to be converted to sheet which is to be shaped by thermoforming to be converted to sheet which is to be employed in indesirably are more viscous than polymers to be employed in indesirably are more viscous than polymers to be employed in indesirably are more viscous than polymers to be employed in indesirably are more viscous than polymers to be employed in index, jection moulding. The former have a lower melt flow or melt index, generally due to a higher molecular weight, than the latter. Compositions according to this invention can be prepared with different melt flow properties by selecting Components "A" and "B" having the appropriate flow properties.

The invention includes also articles made by extrusion or injection moulding from compositions within the specified ranges.

Such articles have satisfactory physical properties, including impact resistance, and are characterized by excellent resistance to chemicals, sometimes referred to as crazing agents, which induce stress cracking in conventional polystyrene or high impact polystyrene, primarily fatty materials such as fatty foodstuffs, e.g., butter or margarine, cooking oil, etc., but also other chemicals, e.g., certain alcohols and hydrocarbons.

Articles made from the specified compositions by extrusion or by injection moulding have a characteristic microstructure which results in their unusual properties. It has been found that in the body of these articles the polystyrene and the polyolefin do not exist as discretely dispersed particles, but as continuous phases which form one interlocking network structure, while the outer surface layer or skin is substantially enriched in polyolefin, thus providing the excellent resistance to fatty organic compounds which is characteristic of the articles of this invention. The block copolymer is believed to act as a mechanical or structural stabilizer which interlocks the polymer structure networks in the body of the articles.

This internal structure is evidenced by the fact that when a shaped composition according to the invention is treated with a solvent such as toluene to dissolve out the polystyrene and at least part of the block copolymer, the undissolved polyolefin remains as a porous structure, generally showing the shape of the original article and in particular showing a continuous or nearly continuous outer surface. In some cases, as in extruded sheet, the inner part may contain insufficient polyolefin to provide a continuous structure throughout after leaching, but this does not affect adversely the desired properties of the article. These articles will be referred to as having a skin layer which is substantially enriched in polyolefin. The thickness of the skin layer is in part a function of the method of manufacturing the article and of the thickness of the article. In a typical article, in cross section through the thickness of the article, at least

the outer 5-10% of the article near the surface is substantially enriched in polyolefin, as determined by leaching or by scanning electron microscopy.

The distribution of the components of the composition which results in the skin layer of polyolefin is attributed to flow phenomena during the forming of the article, such as occur in extrusion and injection moulding. It is thought that the polyolefin, being the lower viscosity component of the mixture, flows more easily than the other components in the region of highest shear, and hence there is some concentration of polyolefin near the walls while the mixture is flowing under pressure. The articles of this invention can be produced on commercially available extrusion or injection moulding equipment.

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In a further modification of this invention, grease-resistant articles are produced in a secondary forming operation, such as thermoforming of sheet produced by extrusion of compositions of this invention.

this invention.

The invention is illustrated in the following Examples, certain of which include for comparative purposes compositions falling outside the scope of the invention and also commercial HIPS and ABS.

Unless otherwise stated, the polymer blends employed in the Examples were prepared by dry-blending all the ingredients and passing the mixture in a single pass through a twin screw extruder which had a screw conventionally employed for extrusion of polywhich had a screw conventionally employed for extrusion of polystyrene and was operated at a maximum melt temperature of about 245°C.

Articles for testing were 2.5 mm thick sheet, prepared from the various compositions by extrusion through a sheet die at conventional conditions for polystyrene extrusion, unless otherwise stated in the text of the Examples.

The compositions illustrated in the Examples were prepared from several different grades of polystyrene homopolymer, impactimproved polystyrene-polybutadiene graft copolymer, polyethylene, polypropylene and S-EB-S copolymer. The following components were employed:

Commercial grades of styrene homopolymer, commonly referred to as crystal grade or general purpose grade of polystyrene (designated "GPS").

Commercial graft copolymers of polybutadiene and styrene,
medium impact polystyrene (designated "MIPS") and high impact
polystyrene (designated "HIPS").

Commercial grades of low density polyethylene (LDPE) and high density polyethylene (HDPE) and several commercial grades of polypropylene (PP).

The significant properties of the thermoplastic components
"A" and "B" employed in the Examples are shown in Table 1.

Mechanical properties shown in Table 1 are specification data
determined on injection-moulded specimens.

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The block copolymer components "C" employed in the Examples are coded BC-1 through BC-6. Copolymers BC-1 through BC-3 are "S-EB-S" polymers, BC-4 and BC-5 are SBS polymers and BC-6 is a two block S-EB polymer, the nominal compositions being as given in Table 2 in terms of the designations code described above.

The proportions of components "A", "B" and "C" employed in the Examples, and the properties of blends are shown in the Tables 3-5.

The properties reported in the Tables were measured by the following test methods:

	following test have	ASTM method
	Property	D-1238
25	Melt flow	D-1525
	Vicat softening temperature	D-638
	Tensile properties	D-1790
	Flexural modulus	D-256
	Izod impact	D-648
30	Heat distortion temperature	D-75
	Rockwell hardness	D-3029
	Dart impact failure (DIF)	atances report

Resistance to attack by fatty substances, reported as "Environmental Stress Cracking Resistance" (ESCR) was determined

by cutting a sample strip from an extruded sheet transverse to the machine direction, clamping the sample over a mandrel which has a constant radius of curvature of 17.75 cm, coating the sample with 50:50 mixture of cottonseed oil and oleic acid, holding the sample in place for 24 hours - at a strain of 0.7% - and thereafter measuring the flex modulus and tensile strength. The values are reported as per cent of the corresponding values of a sample which had not undergone the contact test.

In addition, sample strips coated with said oil mixture were exposed to 6.9 and 13.8 MN/m^2 loads and the time to breaking of the strip reported as time to failure.

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TABLE 1

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Properties of thermoplastic components employed in Examples

											_
			"A"		,				+		
Component						TUDE	HDPF.	PP-1	PP-2	PP-3	
	GPS-1	GPS-2	MIPS	HIPS-1	HIPS-2	מ זענו		· -			
Property					;	*	**	****	5.0***	12***	
Melt flow, 200°C,	***	* ~	* 6	3.5*	11*	3.0	ر. د.ع))			
g/10 min.)						,	c u	150	152	
Vicat softening			5	26	89	95	131	201	1	,	
Do Thempt	103	<u></u>	3	` .	,	10 35	١	28.25	30.35	31.0	
2	α α	51.7	31.7	8.42	19.3	(6.5)				1	
Tensile yield/MN/m	0.00	:		7.00	17.25	ı	27.6	1	1		
2 MM /m2	63.8	51.7	59.6	22.12	\ <u></u>			000	> 100	>100	
Stress at Dream Parl	1		00	35	35	240	1	2))		
ש יחסילים איסירם	α 	N	2	``						,	
PTOIIRE TOTAL						, T	290	1240	1345	1380	
Flexural modulus,	3100	3100	2620	5200	2000	60	<u> </u>	!			
MN/m ²) 	:) 									
120d impact, Joules/											
2.54 cm, notched						ou		1 35	0.8	0.68	
0.63 cm specimen		0.21	1.08	2.03	1.76	break	ı 	`			٦
room temperature	- -	i • •			_	-					
	-	_									

* Condition G
** Condition E
*** Condition L

TABLE 2

			<u>'T'A</u>	Blie E	Ċ		: ~	the
			copolymers Ex	(Component	C)	employed	711	UIIC
Types	of	PTOCK	Ex	kamples		<u></u>		

Types of block	Examples
	Type
Composition	7.5S-37EB-7.5S
BC-1	10S-54EB-10S
BC-2	29S-116EB-29S
BC-3	10S-53B-10S
BC-14	16S-75B-16S
BC-5	
вс-6	64S-38EP

EXAMPLE I - Comparison of preferred blends according to the invention with conventional ABS and HIPS and with blends prepared without HIPS

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The articles of this Example were prepared from the compositions shown in Table 3. Composition I-X is a commercial grade of high impact ABS copolymer and I-Y a commercial high impact polystyrene. Compositions I-A and I-B are preferred blends according to this invention, containing, respectively, 80% HIPS and a blend of 40% HIPS with 40% general purpose polystyrene together with 8% polypropylene and 12% block copolymer. Composition I-Z contained only general purpose polystyrene (no HIPS), together with the same proportions and types of polypropylene and block copolymer as

The main object of this invention is to prepare articles which I-A and I-B. have an impact resistance in the neighbourhood of that of high impact polystyrene and chemical resistance comparable to that of ABS. As shown in Table 3, ABS (I-X) has significantly higher yield and flex strength and somewhat higher heat resistance and impact strength, compared to commercial HIPS (I-Y). The major property in which HIPS is unable to compete with ABS in certain applications is chemical resistance. The articles from composition I-Y performed poorly in the tests of chemical resistance.

Comparing the properties of extruded sheet from compositions I-A and I-B, which are examples of preferred compositions according to this invention, with sheet from I-Y (commercial HIPS) shows that it is possible within the scope of this invention to match the heat resistance, strength and impact properties of HIPS and to

obtain much greater chemical resistance. Comparing the properties of sheet from compositions I-A and I-B, it is seen that by replacing some of the HIPS component with general purpose polystyrene one increases the strength properties while decreasing impact resistance and somewhat decreasing chemical resistance.

Composition I-Z, which contains only general purpose polystyrene and no HIPS, gives sheet with greater strength properties than that from I-A or I-B, attributable to the general purpose polystyrene. However, the resulting impact resistance is in the same range as that of general purpose polystyrene. This composition, therefore, does not show the improvement in impact resistance which is said to be the purpose of invention U.S. 4,013,166 referred to in the discussion of the prior art, and is not within the scope of the present invention.

TABLE 3

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		TABLE 3					_
:	- 77	I-Y	I-A	I	-B	I-Z	_
Composition	I-X		80	1	40	0	
HIPS-1	- ['] '	100	0		40	80	
GPS-1	_	0	8		8	8	
PP-3	-	. 0	12		12	12	1
BC-1	-	0	-		<u>-</u> :	-	
ABS	100						
3							
Property	+			1	5.3	5.3	1
Melt flow, 200°C.	d 1.2	3.8	4.5	'	7.5		
Vicat softening temp., C	102	98	.\ 98	3	94	104	
West distortion		. *					
temp., 1.82 MN/m ² , annealed	91	88	8	9	91	92	
Tensile yield,	42.8	3 26.	0 18	3.8	25.2	38.9	
MN/m					24.	6 34.0	
Ultimate yield, MN/m ²	39.	2 23.	3 2	8.0	٠٠٠		
Tensile elongation, %	17	3		54	36	9	

TABLE 3 (cont'd)

ABLE 3 (cont'd)									٦
* 4.5 am	I-X	I-Y	I-	-A	I-	B !	I-	Z. 	$\frac{1}{2}$
Composition Flexural strength, MN/m ²	82	48.25	38	.6	. 50	.0	71.	7	
Flexural modulus, MN/m ²	2830	2150		1550	20	00	256		
Hardness, Rockwell R	114	103	;	72		91	11	O _J †	
Izod impact, Joules/2.54cm, notched 0.63cm specimen (a) room temp29°C	2.4 1.35			2.3 0.98		.83 .64		.32 .3 ¹ 4	
DIF, Joules/ 2.54 cm room temp. _40°C			05	596 427		515 224	20	197).3	,
Environmental stress crack- ing resist- ance % retent of flex			64	· 10	0	93		0	
% retent. of tensile yield			81	. 9)2	94		0	
% retent. of elongation			<1	:	46	26		. 0	
6.9 MN/m ² load time to fail	,	; :	1.7	5 <u>a</u>	ays	35 1	nrs.	2.6 hr	s.
13.8 MN/m ² loatime to fail	d,	2	5 min.	str	ret- es	20	min.	74 mir	a.`

⁽a) Specimen injection moulded

EXAMPLE II - Comparable articles from compositions containing polypropylene and polyethylene

Plaques for testing were prepared by injection moulding from the compositions illustrated in Table 4. The components were blended in a single screw extruder and directly injected into the moulds. Compositions II-A and II-D were prepared with polypropylene, II-B and II-E comparably with low density polyethylene and II-C and II-F comparably with high density polyethylene. Compositions A, B and C contained HIPS as the sole styrenic thermoplastic and D, E and F equal proportions of HIPS and general purpose polystyrene. In each case, the performance properties of the compositions prepared with polypropylene and polyethylene were satisfactory.

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While the articles from compositions II-D and II-E in this case showed relatively low resistance to chemical attack, it was shown in other tests that at least compositions similar to II-D can show excellent environmental stress crack resistance (see Example I-B).

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		II-B	II-	-c T	II-D	II	-E	II-F	
Composition	A-II		<u> </u>	80	40		40	40.	
HIPS-1	80	80	'	0	40		40	40	
GPS-2	0	0		0	12	2	0	0	
PP-3	12 0	12		0	(12	0	
LDPE	0	0		12		o	0	12	
HDPE	8	8		8		8	8	8	·
BC-1		-	1-		1.				
Property		98	+-	100	10)2	101	103	3 .
Vicat softening temp., C Heat distortion temp.,	102			100		89	91		
1.82 M/m ² , anneated,	87	21.	1		İ	Ъ.	29.3		
Tensile yield, MN/m2	21.4		į		i	.2	25.5	5	
Ultimate yield, MN/m	22		-			56	47	7	
manaile elongation, %	76 38		1	38.	4 53	3.3	44.8		52
Flexural strength, MN/m ²	1430			134	5 2	180	196	-	65
Flexural modulus, MN/m ² Hardness, Rockwell R	77		74	7	1	88	7	6	88
Izod impact, Joules/2.54c notched 0.63 cm specimen room temp.	m,	5 2.	85		1	.02	1.3		,
DIF, Joules/2.54 cm room temp.	29	90 41	8	44	1	136	17	1 1	36
Environmental stress cracking resistance 6.9 MN/m ² load, time to fail		16 1	<u>1</u> , <u>1</u> ,	~	75	2	3.	.5	100

EXAMPLE III - Comparison with related composition outside the scope of this invention

Compositions of 80 parts of HIPS-1, 12 parts PP-3, and 8 parts of block copolymers BC-2 through BC-6 (as defined in Table 2) were prepared. All the compositions were injection moulded at a melt temperature of 277°C to give 10 cm x 10 cm x 1.5 cm plaques, which were tested comparably to composition II-A of Example II. The plaques from compositions BC-2 through BC-5 gave falling dart impact resistance values too low to measure (less than 40 Joules/2.54 cm thickness). This contrasts with the value of under and 290 Joules/2.54 cm thickness for general purpose polystyrene and 290 Joules/2.54 cm thickness for plaques prepared from the compositions employing corresponding amounts of BC-1.

The blends with very poor impact resistance showed brittle, mica-like fractures, very similar to blends of pure polypropylene with HIPS. In all these cases, the plaques seemed to separate under stress along the interfaces.

The composition prepared with the 2-block copolymer BC-6 formed plaques which had satisfactory impact resistance. However, when flexed, they cracked very readily along the direction of flex. The article prepared from the 2-block copolymer also showed poor resistance to stress or cracking under the influence of grease.

As a result of the study, it was concluded that block copolymers having significantly higher molecular weights than BC-1
25 are not useful in the composition of this invention and hence
when the block polymer is a S-EB-S polymer the total molecular
weight should preferably be below about 60,000, that of the
styrene blocks about 5,000-10,000 and that of the EB blocks
about 25,000-50,000; that articles prepared with the 2-block copolymer compare unfavourably with those according to the present
invention, having relatively unsatisfactory grease resistance and
poor resistance to flexing.

Unsatisfactory articles also resulted from compositions employing otherwise suitable components outside the specified ranges.

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i,

For example, sheet from a composition containing 80 parts PS-1, 8 parts PP-2 and 12 parts BC-1 was compared with sheet made from compositions I-A and I-B. This sheet was particularly deficient in low impact resistance, compared to conventional HIPS, and therefore not useful for the purpose of the present invention. However, the articles showed satisfactory resistance to chemical

EXAMPLE IV - Different compositions for different forming

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It is known that the rheological properties of thermoplastics affect their performance in different methods of forming. It is therefore desirable to have, for example, plastics of different melt flow properties, depending on whether they are to be used in producing articles by injection moulding or by thermoforming of sheet. For thermoforming, it is desirable to have a more viscous, i.e., low melt flow (higher molecular weight) plastic composition, such as HIPS-1 of the present examples. Compositions I-A and V-A of Table 5 illustrate suitable blends for thermoforming. A high melt flow composition is more suitable for injection moulding, illustrated by composition V-B. Physical properties of these compositions vary about as expected 20

for impact-improved polystyrene compositions of comparable melt flow; the chemical resistance of the compositions is satisfactory. The polypropylene employed in composition V-A is a low flow polymer, more nearly comparable in melt flow and melt viscosity at mixing conditions to HIPS-1 than the polypropylene employed

in I-A. While articles from both of these compositions were satisfactory, it was noted by extraction studies that extruded sheet formed from composition V-A had a more completely interlocked polymer network structure. It was concluded that there is some advantage in employing components A and B for the composition of the present invention which are most nearly identical 30 in viscosity at the conditions of mixing.

19 <u>TABLE 5</u>

	I-A	V-A		V-B	
Composition	80	80			
HIPS-1				80	
HIPS-2		8		8	
PP-1	8				
PP-3	12	12		12	
BC-1					ļ
Property					
Melt flow, 200°C, g/10 min.,	4.5	3.7		8.4	
Cond. G	98	99	1	94	
Vicat softening temp., °C				۰.	1
Heat distortion temp., 1.82 MN/m ² , annealed, C	89	89		85	
Tensile yield, MN/m ²	18.8	17.9	=	13.9	
Tensile yield, MN/m	20.8	19.8		17.4	
Ultimate yield, MN/m ²	54	52		87	
Tensile elongation, %	38.6	35.85		29.65	i
Flexural strength, MN/m ²	1565	1540		1420	
Flexural modulus, MN/m ²	72	76		62	
Hardness, Rockwell R					
Izod impact, Joules/2.54 cm, notched 0.63 cm specimen(a)		2.	1	2.3	
room temp.	2.3	1.		1.06	
DIF, Joules/2.54 cm	595	, 58		590 435	
room temp.	425	38	5	47 <i>)</i>	
Gardner DIF, Joules/2.54 cm	160	17	0	155	
room temp.	111	10		125	
Environmental shear cracking					
resistance	100		93	70 90	
% retent. of flex % retent. of tensile yield	92 46		98 70	36	
% retent. of elongation	5 days	_	days	11 hours	3
6.9 MN/m ² load, time to fail	stret	-	etches	stretche	s
13.8 MN/m ² load, time to fail	stret	THES DOZ			

⁽a) Specimen injection moulded

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CLAIMS

- A composition comprising polystyrene, polyolefin and block copolymers, characterized in that it consists essentially of:
 - A) 60 to 93 parts by weight, per 100 parts of the compositions, of a polystyrene component consisting of 100 to 45% of a thermoplastic styrene-diolefin elastomer graft copolymer with 0 to 55% of thermoplastic styrene homopolymer;
 - B) 2 to 30 parts by weight, per 100 parts of the composition, of polyethylene or polypropylene, and
- C) 5 to 20 parts by weight, per 100 parts of the composition, of a block copolymer X-Y-X where each X 10 is a polystyrene block of 5,000 to 10,000 molecular weight and Y is a hydrogenated polybutadiene block of 25,000 to 50,000 molecular weight, the total molecular weight of the block copolymer being less 15
 - Composition as claimed in claim 1, characterized in that it comprises 70-85 parts by weight component A), 5-20 parts by weight component B) and 8-15 parts by weight component C).
 - Composition as claimed in claim 1 or 2, characterized in that the weight ratio of component C) to component B) is in 20 the range 0.5:1 to 2:1.
 - Composition as claimed in claim 1, 2 or 3, characterized in that the block copolymer X-Y-X component C) is produced by selective hydrogenation of a precursor block copolymer X-Y'-X wherein Y' represents a polybutadiene block.



EUROPEAN SEARCH REPORT

Application number

EP 79 20 0143

	DOCUMENTS CONSIDERED TO BE RELEVANT	Relevant	CLASSIFICATION OF THE APPLICATION (Int. Cl. ²)
ory	Citation of document with indication, where appropriate,	to claim	C 08 L 25/04 55/02
	DE - A - 2 003 916 (BASF) * Claims; page 2, paragraph 7; page 3, paragraph 1; page 3, paragraph 5; page 4, paragraph 1 *	1-4	55/02
			TECHNICAL FIELDS
			SEAHCHED (III.O.)
			C 08 L 25/00 25/02 25/04 25/06 25/08 25/10 25/12 25/14 25/16 25/18 55/02
			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background
			O: non-written disclosure P: intermediate document T: theory or principle underly the invention E: conflicting application D: document cited in the application L: citation for other reasons
	drawn un for all C	claims	&: member of the same partamily. corresponding docume
	The present search report has been drawn up for all o	arch	Examiner FOUQUIER
	Place of search The Hague 19-06-1979		FOOGOTEN